

2019 DOE VTO Annual Merit Review

Novel Chemistry: Lithium Selenium and Selenium Sulfur Couples

PI: Khalil Amine

Team members: Zonghai Chen and Gui-Liang Xu

Argonne National Laboratory

June 10-13th, 2019

Project ID: bat280

This presentation does not contain any proprietary, confidential, or otherwise restricted information.

Overview

Timeline

- Start - October 1st, 2015.
- Finish - September 30, 2020.
- 80% Completed

Budget

- Total project funding
 - DOE share: \$2000K
- Funding received in FY16&17: \$1000K
- Funding for FY18: \$500K
- Funding for FY19: \$500K

Barriers

- Barriers addressed
 - Polysulfides/polyselenides dissolution and shuttle effect
 - Low electronic conductivity and low active material loading
 - Cycle life

Partners

- Project lead: Khalil Amine
- Interactions/collaborations:
 - **Prof. C. S. Wang (UMD)** Encapsulating S_xSe_y in carbon matrix
 - **Dr. C. J. Sun (APS, ANL)** Mechanism study using in situ XAFS
 - **Dr. Y. Ren (APS, ANL)** Mechanism study using in situ HEXRD
 - **Dr. A. Ngo, and Dr. L. Curtiss (ANL)** AIMD simulation
 - **Prof. Andy Sun (Western University)** ALD and MLD surface coating



Relevance and project objectives

- **Objective:** develop novel S_xSe_y cathode materials for rechargeable lithium batteries with high energy density and long life as well as low cost and high safety.
- **Impact**

This technology, if successful, will lead to:

- A cell with nominal voltage of 2 V and energy density of 600 Wh/kg
- A battery capable of operating for 500 cycles with low capacity fade



Milestones

- Investigate the effect of fluorinated ether electrolytes on Li-Se and Se-S systems with high active material loading (2018-Q4, Completed)
- Explore concentrated siloxane-based electrolytes for Li-Se and Se-S systems (2019-Q1, Completed)
- Develop high performance Li/Se-S batteries using optimized carbon support using concentrated siloxane-based electrolytes (2019-Q1, Completed)
- Computational modeling on the function mechanism of concentrated siloxane-based electrolytes (2019-Q1, Completed)
- Structure evolution of cycled cathode in different electrolytes (2019-Q2, Completed)
- In-operando X-ray absorption spectroscopy study on the working mechanism of concentrated siloxane-based electrolytes (2019-Q2, Completed)
- Parasitic reactions study of Li/Se-S batteries in different electrolytes (2019-Q2, Completed)
- Understanding of the solvation chemistry of concentrated siloxane-based electrolytes (2019-Q3, on-going)



Approach

- Doping Se on S to improve electronic conductivity and increase active material loading
- Investigate the impact of carbon pore structure on the active material loading and performance
- Develop novel electrolyte to suppress dissolution of polysulfide & selenide species
- Use in-operando synchrotron X-ray and spectroscopy probes to understand failure mechanism
- Deploy advanced modeling capability to complement diagnostic results



Collaborations

- Prof. C. S. Wang (University of Maryland at College Park)
 - Encapsulating S_xSe_y in carbon matrix.
- Dr. C. J. Sun (APS, ANL)
 - Mechanistic study on the capacity fade of Se and S_xSe_y cathodes using in situ XAFS.
- Dr. Y. Ren (APS, ANL)
 - Mechanistic study on the capacity fade of Se and S_xSe_y cathodes using in situ HEXRD.
- Dr. A. Ngo and Dr. L. Curtiss (MSD, ANL)
 - Ab initio molecular dynamics simulation.
- Prof. Andy Sun (Western University)
 - ALD and MLD surface coating



Responses to Previous Year Reviewers' Comments

- No comments from the reviewers



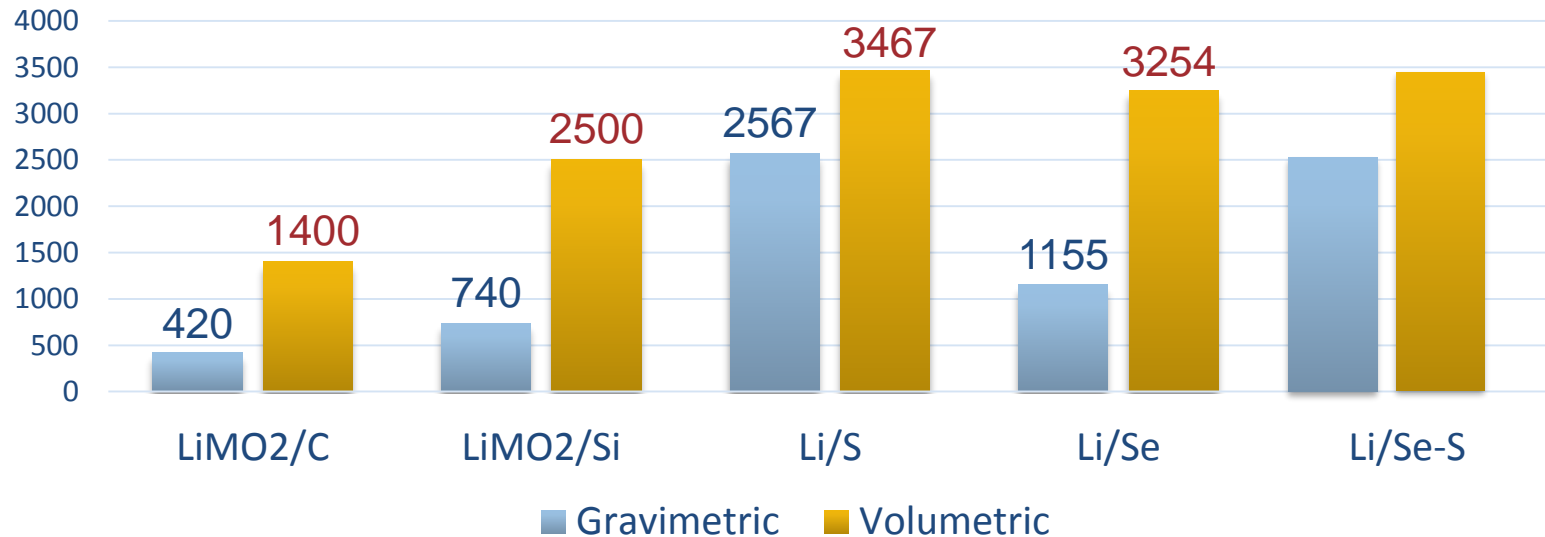
Technical accomplishments

- Enable the use of macroporous carbon for high Se-S loading in the cathode material to increase volumetric energy density using fluorinated ether-based electrolytes
- Explore novel concentrated siloxane-based electrolytes to suppress polysulfides/polyselenides shuttle
- Elucidate the function mechanism of concentrated siloxane-based electrolytes on the solid-solid lithiation chemistry of Se-S cathodes using multiple diagnostic tools



Motivation

Energy density chart



Selenium sulfur systems can lead to:

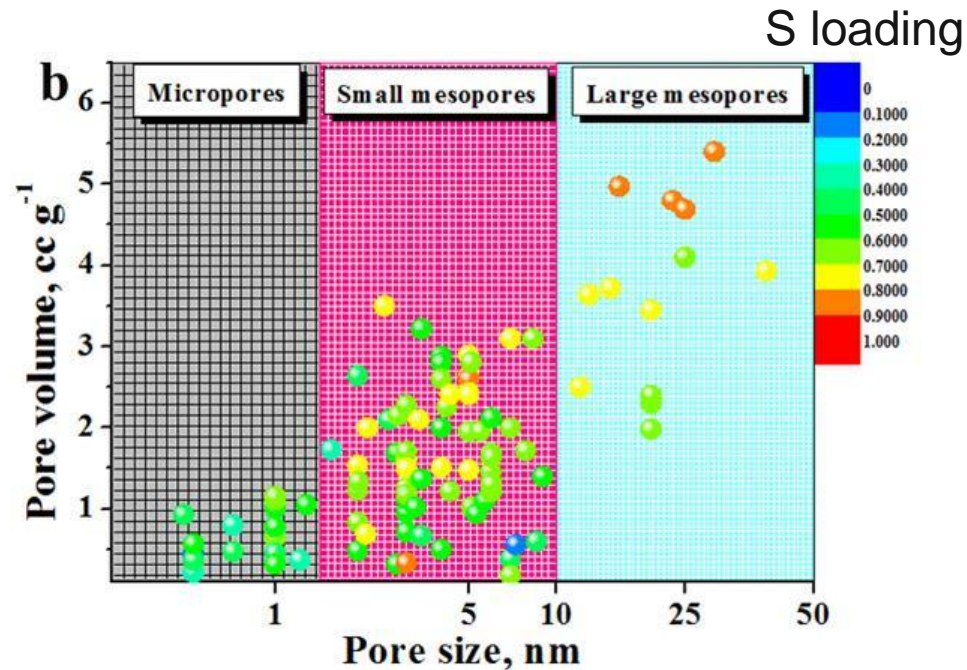
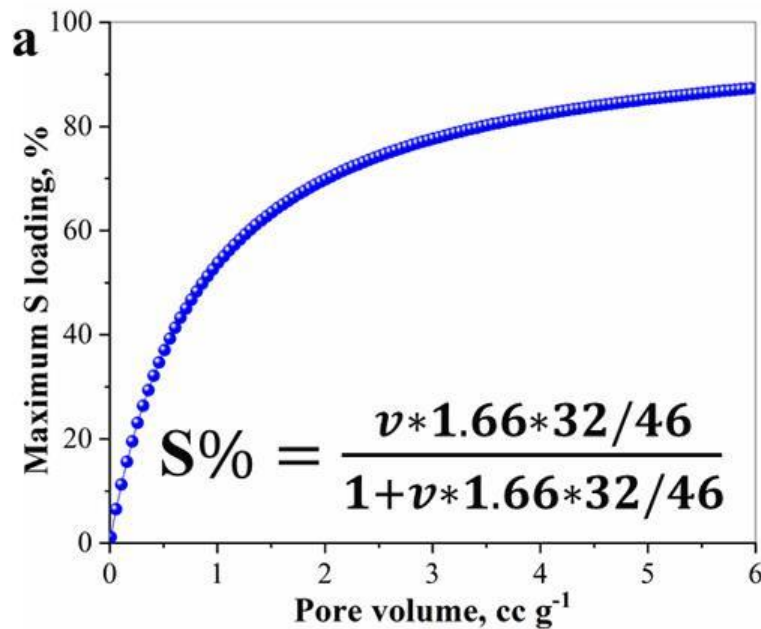
- Comparable energy density to Li/S battery
- High electrical conductivity (1E^{-3} vs. 5E^{-28} S/m for S)
- High active material loading, leading to high volumetric energy density



Correlation between pore structures of host materials and sulfur loading

Estimation of the maximum S loading in pore volume considering volume change from S to Li_2S

Reported S loading with different carbon host materials



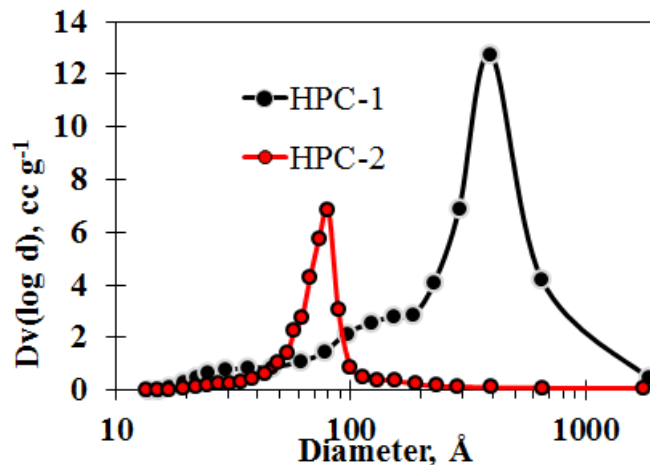
Xu, Amine *Adv. Energy Mater.* 2018, 1802235

- Carbon with high pore size and high pore volume can lead to high maximum S loading



Two highly porous carbon (HPC) are used to investigate the pore structures effect on the loading and performance

Pore size distribution



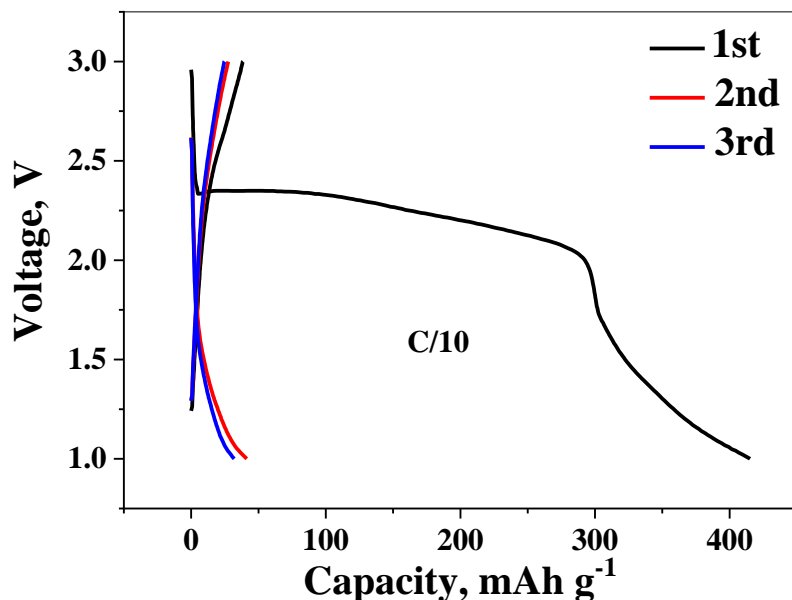
* Considering volume change from S to Li₂S

	Pore size	Specific surface area, m ² /g	Pore volume, cc/g	Maximum S-Se loading	Maximum S-Se loading*
HPC1	40 nm	1446	6.053	92.4 wt.%	87.5 wt.%
HPC2	8 nm	818	1.464	74.5 wt.%	62.5 wt.%



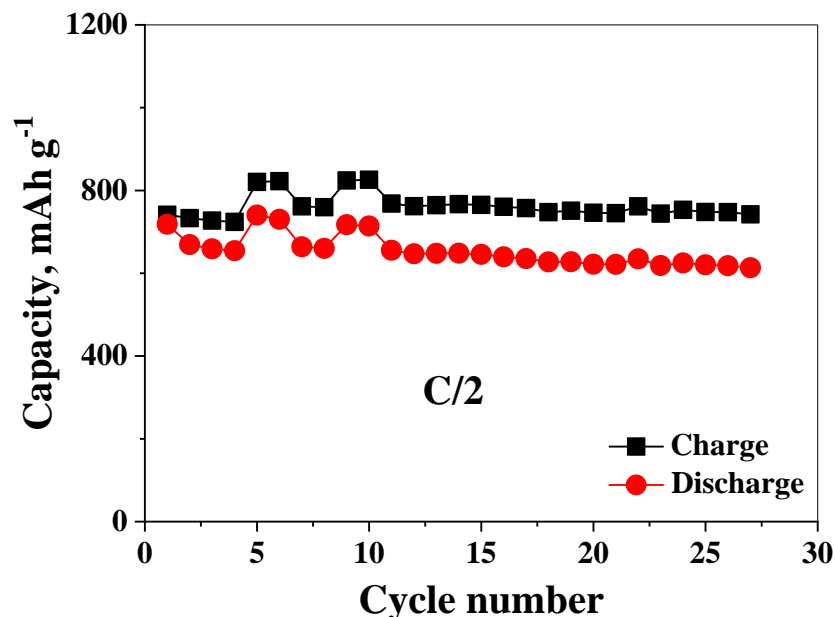
$S_{22.2}\text{Se}/\text{HPC1-85}$ wt.% does not work well in the carbonate and ether based electrolytes

1M $\text{LiPF}_6/\text{EC-DMC}$ (1/1, v/v)



- $S_{22.2}\text{Se}/\text{HPC1-85}$ wt.% composite does not work in carbonate based electrolytes due to nucleophilic reactions between Li_2S_n with carbonate solvents

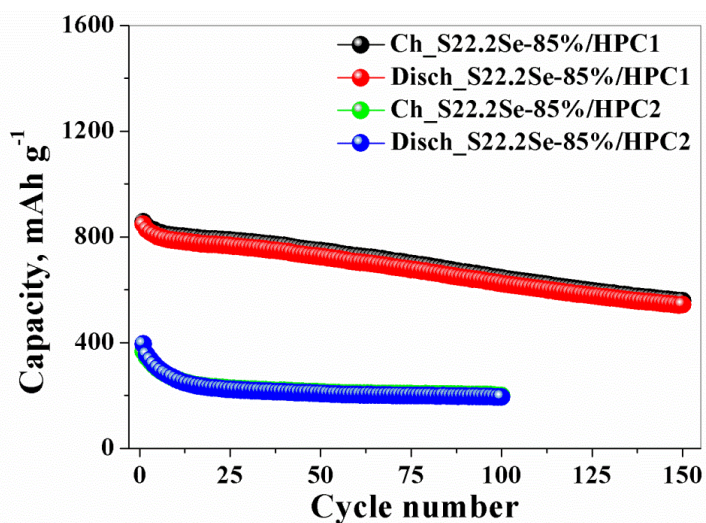
1M $\text{LiTFSI}/\text{DOL-DME}$ (1/1, v/v)+0.2M LiNO_3



- $S_{22.2}\text{Se}/\text{HPC1-85}$ wt.% composite suffers from severe shuttle effect in the conventional ether based electrolytes due to poor confinement effect of macroporous carbon

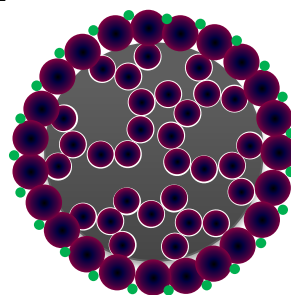


Fluorinated ether electrolytes enable the use of macroporous carbon for high loading cathodes to increase the volumetric energy density



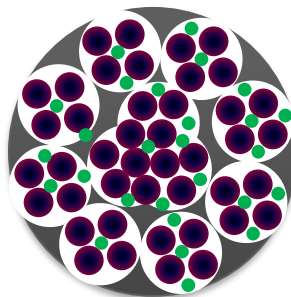
Electrolytes: 1M LiTFSI/DOL-HFE (1/1, v/v)+0.2M $LiNO_3$

$S_{22.2}Se$ /HPC2-85 wt.%



Because of low pore volume, excess $S_{22.2}Se$ was deposited on the outer surface of HPC2, blocking the electron and lithium ion transfer (low capacity)

$S_{22.2}Se$ /HPC1-85 wt.%

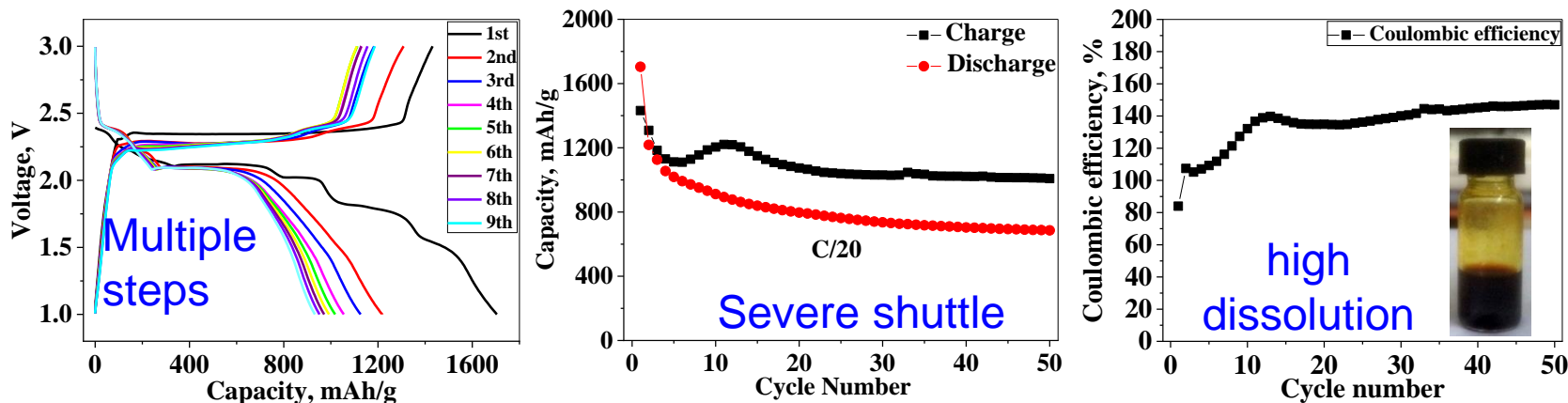


The high pore volume of HPC1 can allow the infusion of high loading $S_{22.2}Se$ within the pores, ensuring electron and lithium ion transfer (high capacity)

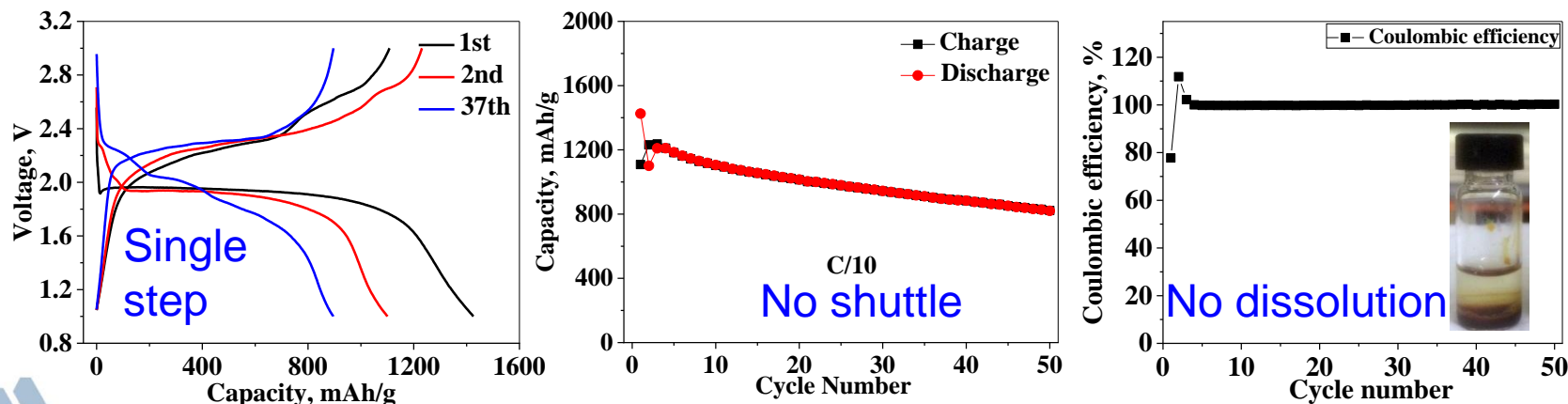


Use of novel concentrated siloxane-based electrolytes to suppress shuttle effect of Se-S cathodes

Se-S/carbon-45 wt.%, 1M LiTFSI/DOL-DME (1/1, v/v)+0.2M LiNO₃

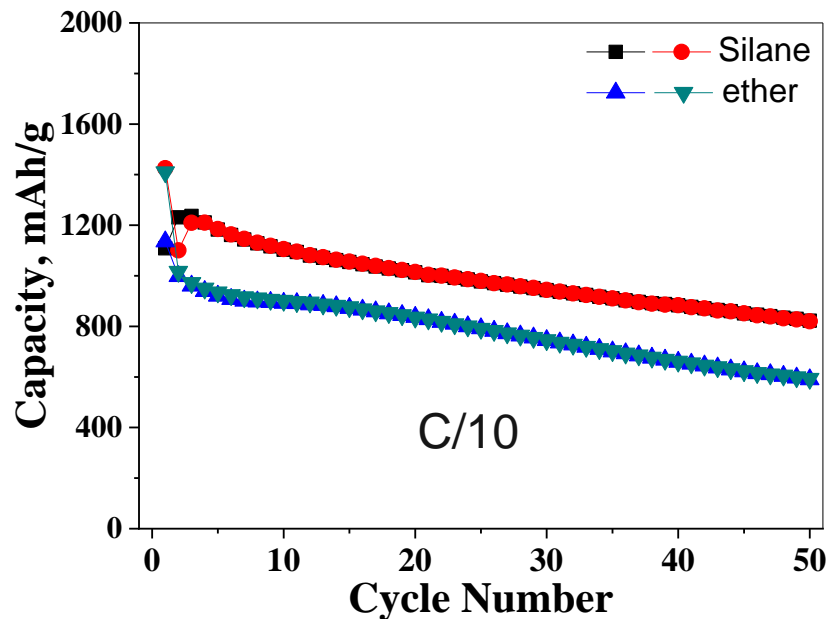


Se-S/carbon-45 wt.%, concentrated siloxane-based electrolytes

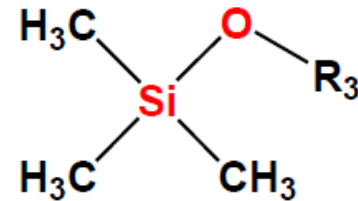


Concentrated siloxane-based electrolytes show higher reversible capacity than concentrated ether electrolytes due to its excellent wetting property

Electrode: Se-S/Carbon-45 wt.%



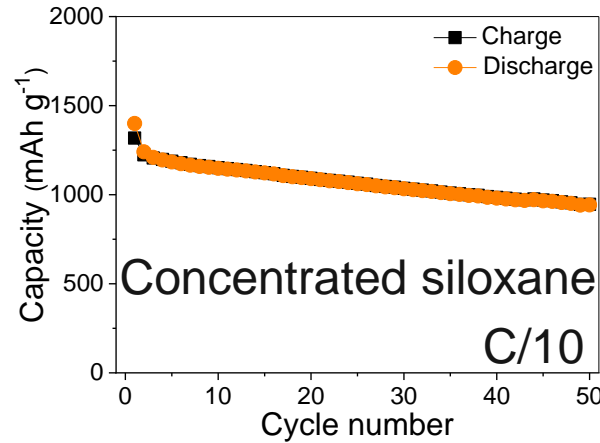
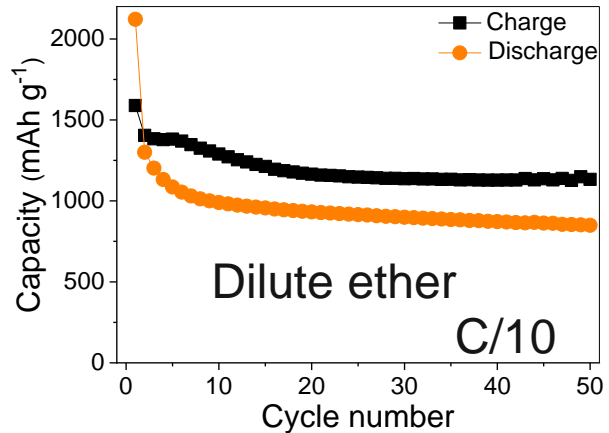
Structures of siloxane



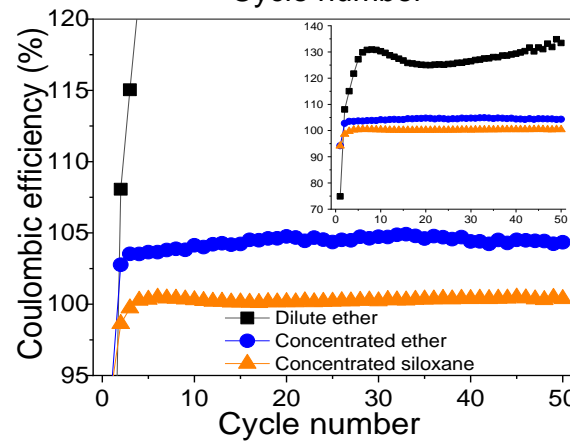
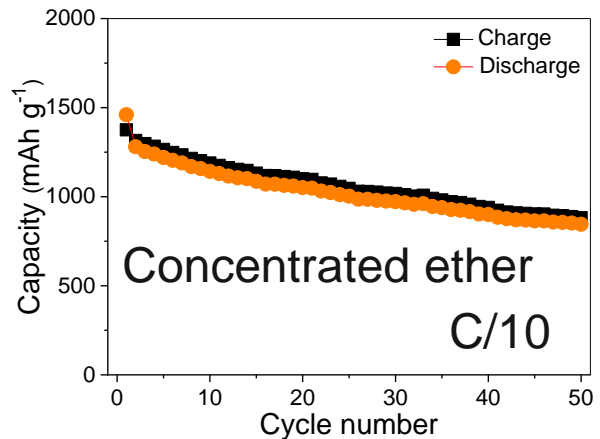
Low viscosity-comparable with carbonate electrolyte



Combination of macroporous carbon and concentrated siloxane-based electrolytes can further improve the electrochemical performance with high loading (S/HPC1-70 wt.%)



No shuttle

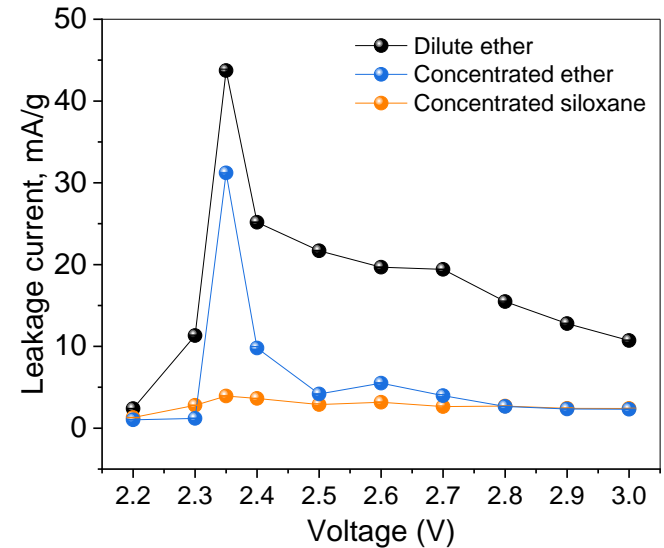
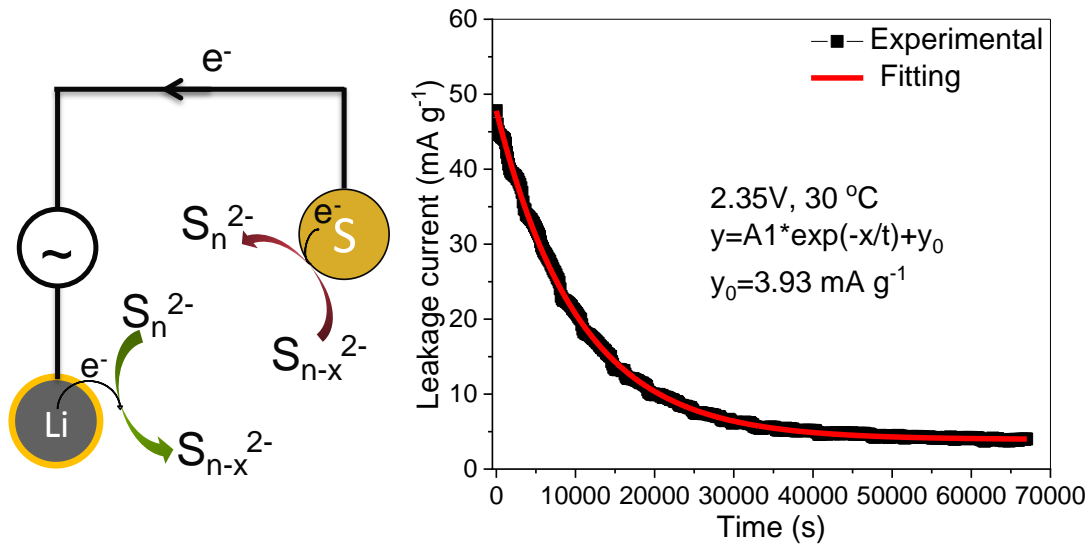


Higher coulombic efficiency value means more severe shuttle effect

Shuttle effect: Concentrated siloxane < Concentrated ether << Dilute ether



Parasitic reactions study using home-built leakage current measurement systems show that S/HPC1 composite has very low leakage current in concentrated siloxane-based electrolytes, indicating No shuttle effect

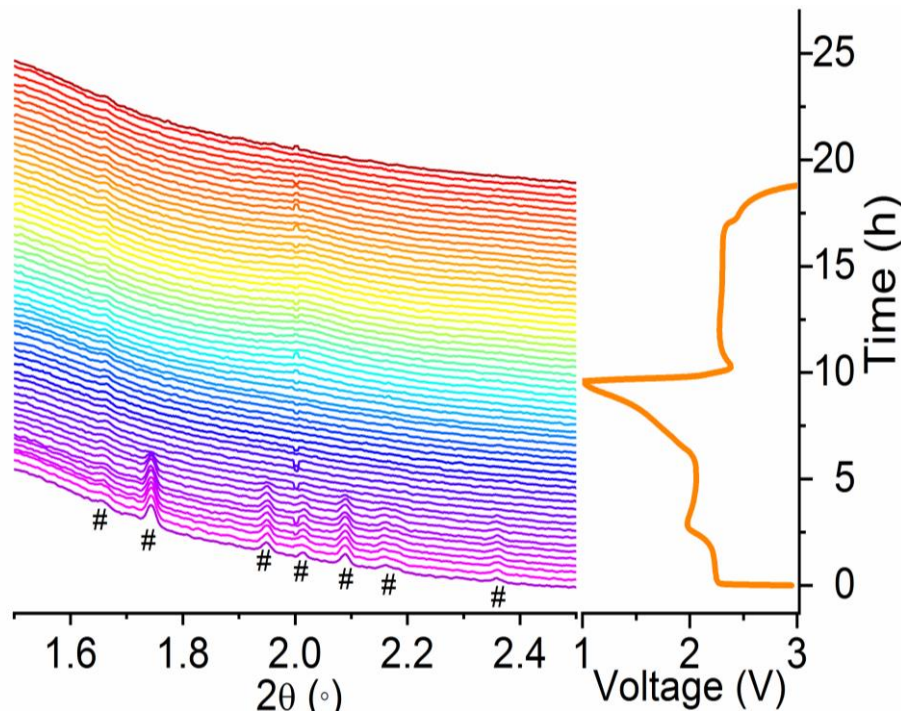


Leakage current: Concentrated siloxane <<Concentrated ether <Dilute ether

The cells were discharged/charged for 2 cycles and then charged to a different potential and held for 20 h to obtain the equilibrium current. The measured leakage current (i) is proportional to the reaction rate of the parasitic reactions between the polysulfides/polyselenides and Li anode during charge.



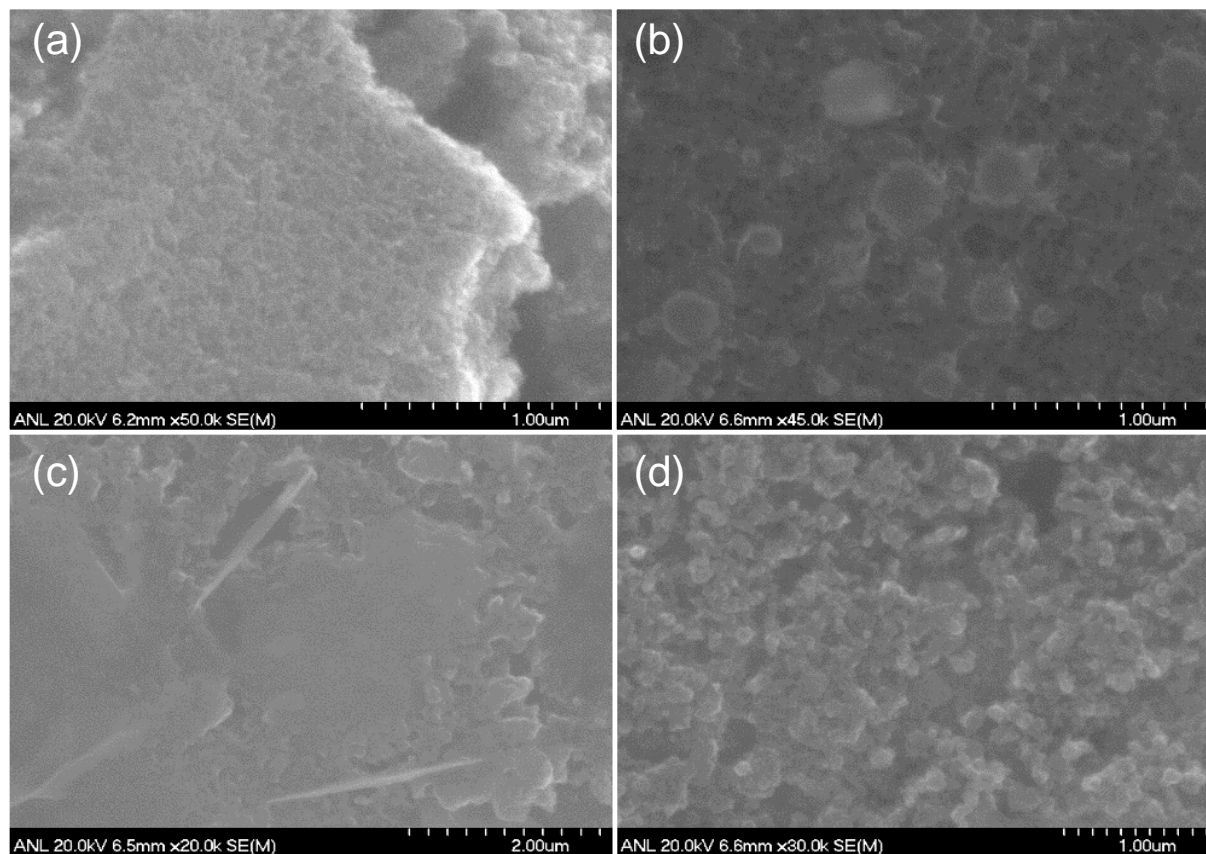
In situ high energy X-ray diffraction (HEXRD) showed that there is no formation of crystalline Li_2S for S/HPC1-70 wt.% composite during cycling in concentrated siloxane electrolytes



In situ HEXRD results showed that crystalline sulfur was converted to amorphous Li_2S during discharge process



Morphology of S/HPC1-70wt.% cathode before and after cycling in different electrolytes



(a) pristine S/HPC1 electrode: highly porous carbon structures

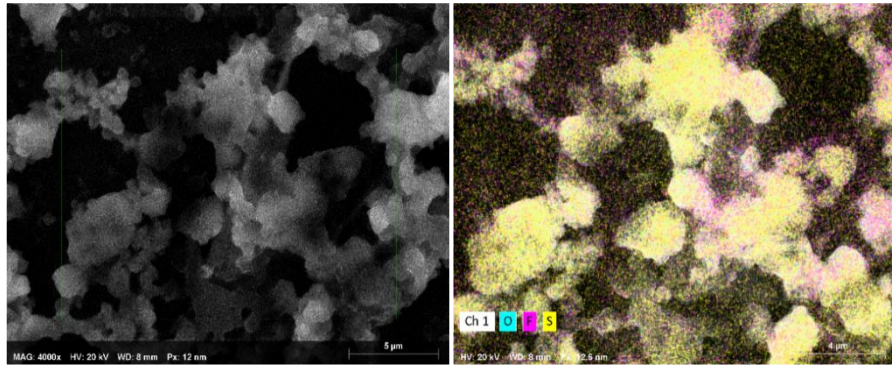
(b) cycled S/HPC1 electrode in dilute ether: formation of crystalline Li_2S

(c) cycled S/HPC1 electrode in concentrated ether: formation of Li_2S flake

(d) cycled S/HPC1 electrode in concentrated siloxane: no formation of crystalline Li_2S

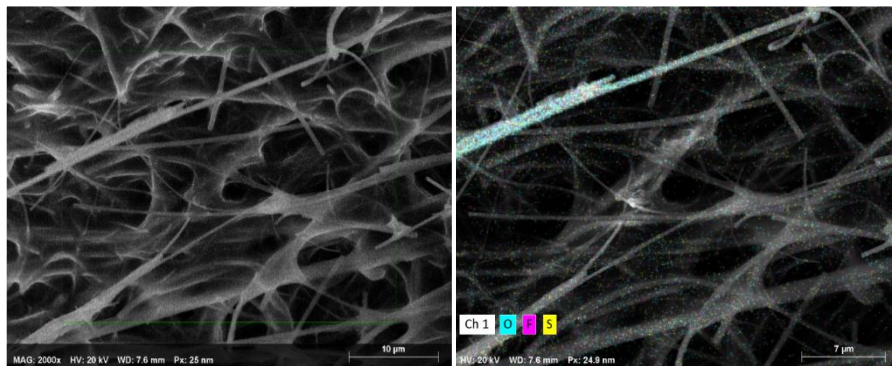
Morphology and composition of cycled separator in Li-S/HPC1-70 wt.% cells using different electrolytes

Dilute ether



Trapping of Li_2S crystals on the separator during cycling in the dilute ether electrolytes

Concentrated siloxane

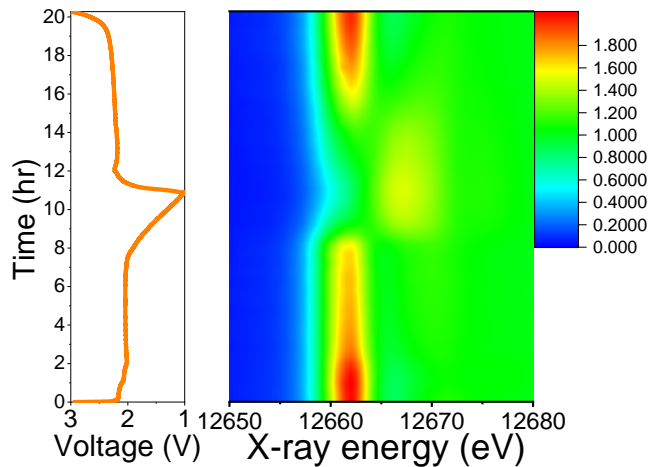


No trapping of Li_2S crystals on the separator during cycling in concentrated siloxane electrolytes

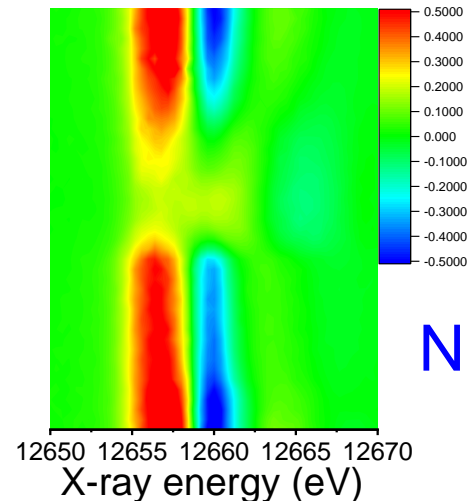


In situ X-ray absorption near edge spectroscopy (XANES) characterization clearly confirmed no shuttle effect of polysulfides/polyselenides (no dissolution)

Se K-edge XANES Spectra



First Derivative of Se XANES



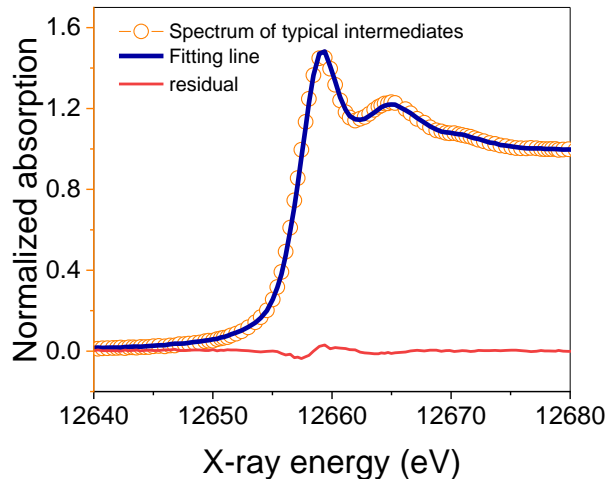
No energy shift

- Se K-edge position did not show clear shifts (no reduction of Se-S take place, no dissolution), but the absorption intensity decreased with discharging and increase during charging

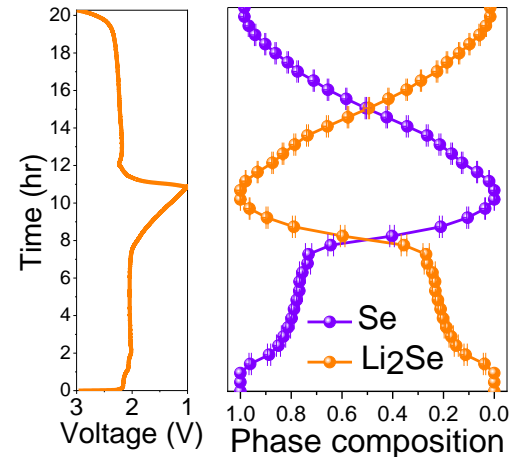


Bypassing the formation of $\text{Li}_2\text{Se}_x (x>1)$ during cycling in concentrate siloxane-based electrolytes

Typical spectrum fitting using Se-
 Li_2Se two-phase transition mode



Linear combination fitting
results of Se XANES

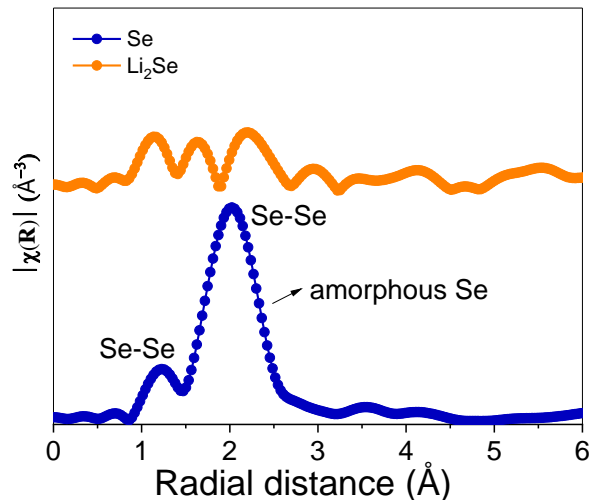


- Li_2Se is formed and increasing in composition with discharge, then oxidized to Se with charge
- Se and Li_2Se two phase fitting leads to decent results

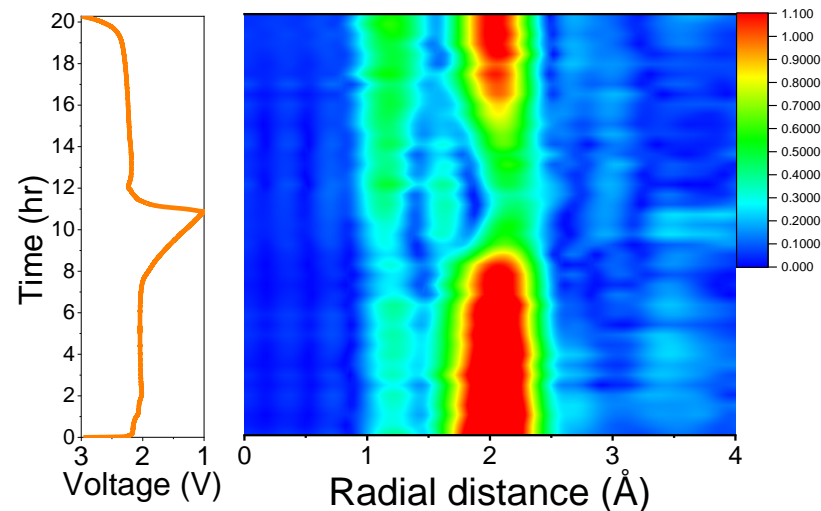


Using extended X-ray absorption fine structure (EXAFS) to probe the local structure evolutions of Se during cycling in concentrated siloxane-based electrolytes

EXAFS Se K-edge data of amorphous Se and Li_2Se



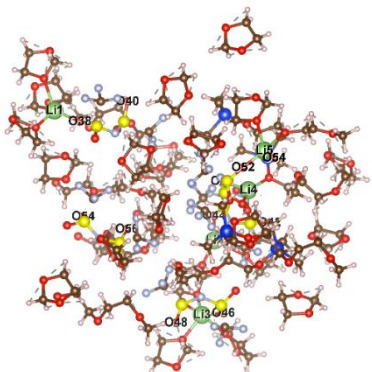
Contour plot of in situ EXAFS Se K-edge data



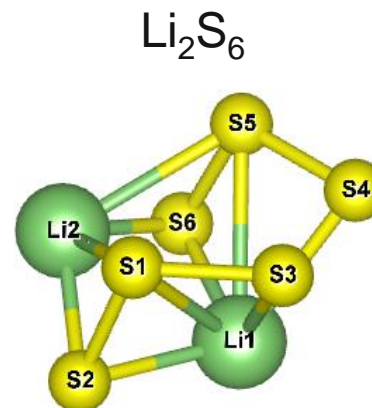
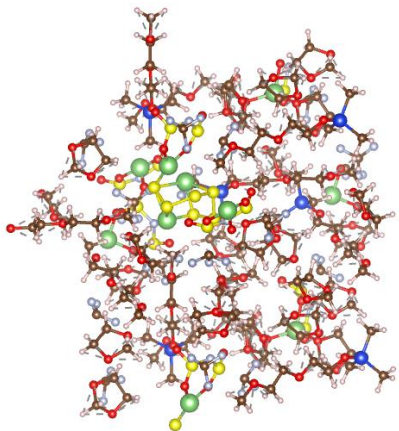
- Se and Li_2Se showed different bond distance features in the Se K-edge EXAFS
- Amorphous Li_2Se formed at the end of discharge
- Amorphous Se re-formed at the end of 1st charge process

Ab initio molecules dynamic simulation shows that there is no interaction between polysulfides and concentrated siloxane-based electrolytes

AIMD Optimized structure of concentrated siloxane-based electrolytes



Structure snapshot of Li_2S_6 in concentrated siloxane-based electrolytes



$\Delta G=2.4936$ eV, indicating the interaction between Li_2S_6 and concentrated siloxane-based electrolytes is unfavorable (high energy barrier)

Proposed Future Work for FY 2019 and FY2020

- FY 2019 Q3 Milestone:
 - Modify the electrode/electrolytes interface using atomic layer deposition and molecular layer deposition
- FY 2019 Q4 Milestone:
 - Interfacial understanding on the Li/Se-S batteries in different electrolytes
- FY2020 work proposed
 - Develop high electrode areal loading Se-S systems (6mg/cm²)
 - Investigate Li stripping/plating behavior in concentrated siloxane-based electrolytes

Any proposed future work is subject to change based on funding levels

Remaining Challenges and Barriers

- The areal loading of Se-S cathodes need to be improved to further increase the volumetric energy density through optimizing cathode structures
- The cathode-electrolyte interfacial chemistry need to be further understood and tailored by surface modification and the use of advanced electrolyte
- Li metal need to be protected to enable reversible Li stripping/plating and prevent Li dendrite formation

Summary

- Fluorinated ether-based electrolytes could enable the use of macroporous carbon with high pore volume for high loading cathodes to increase volumetric energy density
- Novel concentrated siloxane-based electrolyte was explored to suppress polysulfides/polyselenides shuttle
- The interactions between polysulfides and concentrated siloxane-based electrolytes are simulated by *ab initio* molecular dynamics
- The (de) lithiation chemistry of Se-S cathodes was understood by multiple diagnostic tools